**Indications of Transformation Products from Hydraulic Fracturing Additives in Shale Gas Wastewater**

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The boom in hydraulic fracturing operations to tap unconcentional natural gas resources like shale gas is leading to vast volumes of wastewater (Lutz 2013). However, concerns about the adequate disposal of these wastewaters have been raised (Gregory 2011, Ferrar 2013). It is not only the multitude of fracturing additives and geogenic substances which are brought back to the surface in flowback and produced water. Also transformation products may appear. On the one hand, some fracturing additives are, by their chemical nature, prone to reaction in the subsurface (strong oxidizers, delayed acids, delayed breakers). On the other hand transformation reactions are favoured by the presence of elevated temperatures and salinity (Elsner & Hoelzer, in prep.). Knowing more about the substances present in the vast and rising amounts of shale gas development wastewater is, therefore, crucial to identify risks for human health and the environment, and to design strategies for adequate treatment. Presently, these processes are, however, poorly understood and not reported in literature.

We have targeted this research gap by performing HR-GCxGC-TOF-MS measurements with strict confidence assignments alongside targeted and non-targeted GC-FID and GC-MS measurements on wastewater samples from unconventional natural gas development in the Fayetteville Shale. Our results reveal a heterogeneity of the samples, however, with recurrent features like the multitudes of hydrocarbons or a homologous row of carboxylic acids. Archaean core lipids bear potential to be used as a shale fingerprints. Additionnally, we found strong evidence for halogenated compound occurrence in flowback and produced water samples: brominated, iodated and chlorinated alkanes, halogenated methanes and acetones as well as chloromethyl alkanoic acids. Halogenated compounds are barely used in fracturing applications implying that these detected substances are transformation products. Reaction mechanisms are brought forward to explain the formation of halogenated alkanes. Chloromethyl alkanoic acids, in turn, may alternatively serve as delayed esters, thus being tentative fracturing additives.

We conclude that certain halogenated hydrocarbons should be incorporated in shale gas wastewater monitoring concepts because they may be putative transformation products and potential fracking additives. With regard to the heterogeneity of fracturing procedures, additives and bedrocks, there may be more additional types of metabolites emphasizing the need for further research.